

-3-

Description

The present invention is concerned with the use of acid group-containing, thermostable, hydrophilic condensation products of aldehydes and ketones.

5 The condensation of ketones with aldehydes has long been known. In its end stage, it leads to water-insoluble resins. The use of sodium sulphite as an alkaline catalyst, on the one hand, and as substance introducing acid groups, on the other hand, makes
10 possible the formation of water-soluble condensation products which are suitable, for example, as additives for inorganic binding agents for the improvement of their properties.

 Thus, e.g. from DE-AS 2 341 923 are known readily
15 water-soluble condensation products of cycloalkanones and formaldehyde, with the use of sodium sulphite as substance introducing acid groups. However, a disadvantage of these condensation products is their low thermal stability. Thus, e.g. in the case of the con-
20 centrating of a solution of cycloalkanone-formaldehyde condensation products, even under mild conditions (about 50°C.), substantially water-insoluble, powdery compounds are already formed; other sulphonic acid-modified formaldehyde condensation products, for example based
25 upon urea, also decompose at temperatures at the boiling point of water. Therefore, these condensation products cannot be used at high temperatures such as occur e.g. in mineral oil technology in the case of deep drillings.

30 From CH-A 303 371 are known ketone-aldehyde condensation products which are sulphonated. They are used in leather tanning. Furthermore, from DE-A 2 831 613 are known ketone-aldehyde condensation products in the production of which salts were added
35 in catalytic amounts which contain as anion an SO_2 or

-4-

CH₃OSO group. These products are mentioned as lacquer raw materials, adhesive raw materials, binding agents for printing colours, solutions for the impregnation of textiles, for Indian inks and inks, as well as
5 confectioning adjuvants for chemicals, such as e.g. prilling of fertilisers. From US-PS 2 641 591 are known acetone-formaldehyde condensation products which are suitable for textile treatment.

Furthermore, from DE-OS 2 524 199 and Chemical
10 Abstracts reference 91; 145 079 W (SU 668 913) and 98; 220 863 X (SU 983 101), it is known to use ketone-formaldehyde resins not modified by acid groups as concrete additives. These resins serve only for the increase of the pressure and acid strength, whereby one
15 adds them, together with a hardener, to the mortar or cement. Due to the absence of the acid groups, these condensation products display fundamental structural differences towards acid group-carrying, thermostable hydrophilic condensation products. The resins not
20 modified by acid groups serve, by the formation of a solid resin structure, the improvement of strength. However, they display no surface-active action like the acid-modified resins and have, therefore, no properties resulting therefrom, such as dispersing/
25 liquefying or retention or thickening action.

From DE-OS 2 657 453, it is known to use water-soluble ketone-formaldehyde sulphine reaction products for the preparation of dyestuffs.

Therefore, it is the task of the invention to make
30 available thermostable products which, even at high temperatures, are suitable e.g. as additives for the improvement of the properties of aqueous systems. This task is solved with the subject of the present invention.

The subject of the invention is the use of acid
35 group-carrying thermostable, hydrophilic condensation

products of

1. aldehydes and
 2. symmetrical or asymmetrical ketones with acyclic aliphatic, araliphatic and/or aromatic radicals,
- 5 whereby, however, at least one radical is a non-aromatic radical,
- as dispersion agents for inorganic binding agent suspensions and solutions, for aqueous kaolin or clay suspensions and for oil-water-coal suspensions, as
- 10 thickening agents, retention agents and/or liquefaction agents, especially for aqueous systems.

The condensation products used according to the invention possess, surprisingly, a high thermostability. In general, they are stable up to temperatures of at

15 least 300°C. The thermostability is also retained in the presence of water.

As acid groups, the condensation products used according to the invention preferably contain carboxyl, phosphono, sulphino and, in particular, sulpho groups,

20 whereby these groups can also be attached via nitrogen or oxygen or via N-alkylene or O-alkylene bridges and are then, e.g. sulphamido, sulphooxy, sulphoalkoxy, sulphinoalkoxy or also phosphonooxy groups. An alkyl moiety in these radicals preferably possess 1 to 5

25 carbon atoms and is especially methyl or ethyl. The condensation products used according to the invention can also contain two or more different acid groups.

The radical R in the aldehydes R.CHO can be hydrogen, an aromatic or non-aromatic (cyclic or

30 acyclic) carbo- or heterocyclic radical or also an araliphatic radical, in which the number of carbon atoms or of carbon and heteroatoms is preferably 1 to 10. Aromatic radicals are e.g. α - or β -naphthyl, phenyl or furfuryl, araliphatic radicals e.g. benzyl or phenethyl,

35 non-aromatic radicals e.g. cycloalkyl and especially

-6-

alkyl radicals, preferably with 1 to 6 carbon atoms, such as e.g. methyl, ethyl, propyl, butyl. The aliphatic radicals can also be branched or unsaturated and are then e.g. vinyl.

- 5 The aldehydes can also be substituted by one or more substituents which do not impair the condensation reaction, such as e.g. by amino, hydroxyl, alkoxy or alkoxy carbonyl groups, and/or also by the acid groups present in the condensation products. There can also be
10 used aldehydes with more than one aldehyde group, e.g. di- or trialdehydes, which, as a result of their increased reactivity, can be especially expedient in some cases. E.g. in the case of the lower saturated aldehydes, such as formaldehyde or acetaldehyde, there
15 can also be used the polymeric forms (e.g. paraformaldehyde or paraldehyde).

- Examples for saturated aliphatic aldehydes are formaldehyde (or paraformaldehyde), acetaldehyde (or paraldehyde), butyraldehyde; for substituted saturated
20 aliphatic aldehydes 3-methoxypropionaldehyde, acetaldo; for unsaturated aliphatic aldehydes acrolein, crotonaldehyde, furfural, 4-methoxyfurfural, propargylaldehyde; for dialdehydes glyoxal, glutardialdehyde. Formaldehyde is especially preferably used as aldehyde.

- 25 Ketones employed for the condensation products used according to the invention are symmetrical or asymmetrical ketones with acyclic aliphatic, araliphatic and/or aromatic hydrocarbon radicals, whereby, however, at least one radical is a non-aromatic radical. The
30 hydrocarbon radicals preferably possess 1 to 10 carbon atoms.

- Acyclic aliphatic radicals are straight-chained or branched, unsaturated or preferably saturated alkyl radicals, such as e.g. methyl, ethyl, propyl, butyl,
35 isobutyl, nonyl. Araliphatic radicals are e.g. benzyl

-7-

or phenethyl, and aromatic radicals are e.g. α - or β -naphthyl and especially phenyl.

The ketones can also be substituted by one or more substituents which do not impair the condensation reaction, such as e.g. by amino, hydroxyl, alkoxy or alkoxy-carbonyl groups, and/or also by the acid groups contained in the condensation products.

Examples for saturated acyclic ketones are acetone, methyl ethyl ketone, methyl isobutyl ketone; for substituted saturated acyclic ketones methoxy-acetone, diacetone alcohol, acetoacetic acid ethyl ester; for unsaturated aliphatic ketones methyl vinyl ketone, mesityl oxide, phorone; for araliphatic ketones acetophenone, 4-methoxyacetophenone, 4-acetylbenzene-sulphonic acid; for diketones diacetyl, acetylacetone, benzoylacetone.

The aldehydes and ketones are usable in pure form but also in the form of compounds with the substances introducing the acid groups, e.g. as aldehyde-sulphite adduct or as hydroxymethanesulphinic acid salt. Two or more different aldehydes and/or ketones can also be used.

The total number of carbon atoms or possibly of carbon atoms and heteroatoms in the aldehydes and ketones used according to the invention is so chosen that the hydrophilic character of the condensation products is maintained. Therefore, it is also dependent upon the number of acid groups in the condensation product but also upon the ratio of ketone/aldehyde. The preferred total number amounts for the aldehydes to 1 to 11, for the ketones from 3 to 12.

In general, the mole ratio of ketones/aldehydes/acid groups amounts to 1/1 to 6/0.02 to 2, whereby, however, variations are also possible depending upon the special purpose of use.

-8-

Because of their properties, the condensation products according to the invention are used as dispersing agents for inorganic binding agent suspensions and solutions, for aqueous kaolin or clay suspensions and for oil-water-coal suspensions, as thickening agents, retention agents but also as liquefaction agents, especially for aqueous systems.

The desired properties can thereby be controlled by suitable choice of the starting compounds and of the mole ratios. As examples for aqueous systems in which the products according to the invention can be advantageously used, there are mentioned: inorganic binding agent suspensions and solutions, dispersion agents for oil-in-water emulsions, aqueous kaolin or clay suspensions and oil-water-coal suspensions. As a result of their high thermostability, the condensation products according to the invention are especially well suited as additives for inorganic binding agents. The products according to the invention are so stable that they can be ground with clinker in the cement mill without loss of activity. As dispersion agents, they are suitable, for example, for the production of flowing concrete or tile-adhesive materials and, as a result of their good thermostability, especially also for the liquefaction of deep drilling cement mixtures, for which purpose a high temperature stability is necessary because of the high temperatures which arise. As retention agents, they are suitable for the production of slurries of hydraulic binding agents which display good water retention properties (e.g. in the case of deep drilling cement slurries or in the case of liquid adhesives) and, as thickening agents, they are very well suited, e.g. in mineral oil technology for increasing the viscosity of aqueous solutions and suspensions.

-9-

The condensation products are preferably used in the form of solutions or dispersions, especially in the form of aqueous solutions or dispersions. The solids content of these compositions amounts, in general, to 10 to 70, especially 20 to 50 wt.%.
5

There can be used two or more condensation products with the same, similar and/or also different effectiveness or their mixtures with one or more known additives with the same, similar and/or different effectiveness, such as e.g. mixtures with known dispersing agents, tensides or concrete additives. In this way, the properties of the end products can often be additionally changed or differentiated.
10

The predominating properties of the condensation products used according to the invention depend especially upon the nature and the mole ratio of aldehydes/ketones/acid group-introducing compounds. The hydrophilic character decreases with decreasing proportion of acid groups, whereby, as a rule, in the case of a value of 0.15 mole, complete water solubility is no longer to be achieved. For dispersing agents and liquefiers, there are preferably suitable formaldehyde, glyoxal and acetone and a ratio of ketone/aldehyde/acid group-introducing compounds of 1 to 0.25 to 2. Surface-active materials are preferable obtained by reaction of aldehydes and ketones with longer alkyl radicals or with aralkyl radicals which contain at least more than 1 carbon atom and a ratio of ketone/aldehyde/acid group-introducing compounds of 1/1 to 6/0.05 to 2. Retention and thickening agents are obtained from aldehydes and ketones with alkyl radicals which contain up to 3 carbon atoms and display a mole ratio of ketone/aldehyde/acid group-introducing compounds of 1/1 to 6/0.2 to 2. By a combination of the conditions preferably employed for the specific properties, e.g. by combination of the
15
20
25
30
35

-10-

nature of the starting materials especially suitable for a particular property with the mole ratio preferred for another nature, mixed properties can also be achieved.

The condensation products used according to the invention can be obtained by reaction of the ketones, aldehydes and acid group-introducing compounds under alkaline pH conditions, whereby one can proceed in the manner of a one-pot reaction. As embodimental forms for the production of the condensation products, the following variants are possible:

- I. Taking the ketone and the acid group-introducing compound and addition of the aldehyde,
- II. Taking the aldehyde and the acid group-introducing compound and addition of the ketone,
- 15 III. Taking the ketone and addition of a mixture of aldehyde and acid group-introducing compound or (e.g. in the case of sulphite) of a compound of the aldehyde with the acid group-introducing compound,
- IV. Taking the aldehyde and addition of a mixture of ketone and acid group-introducing compound or of a 20 compound of the ketone with the acid group-introducing compound, and
- V. Simultaneous taking of aldehyde, ketone and acid group-introducing compound.

25 In the case of Variants I to V, instead of the ketone there can, in each case, also be used a ketone-aldehyde condensation product which contains all or part of the necessary amount of ketone and/or aldehyde.

Generally speaking, the process Variant I is preferred; the process Variant V is especially suitable for 30 the reaction of less reactive components.

In general, the reaction commences even in the case of gentle heating and then proceeds exothermally so that, as a rule, it is cooled. For the achievement of 35 a uniform product or especially in the case of the use of

-11-

less reactive starting products, a post-heating is expedient, which can last for up to several hours.

The reaction is generally carried out at a pH value of 8 to 14, preferably in the range of 11 to 13.

5 The pH value adjustment can take place e.g. by addition of hydroxides of mono- or divalent cations or by taking an acid group-introducing material, e.g. of sodium sulphite, which is hydrolysed in aqueous solution with alkaline reaction.

10 The reaction can be carried out not only in homogeneous but also in heterogeneous phase. As a rule, as reaction medium water or a mixture with water is used, whereby the proportion of the water preferably amounts to at least 50 wt.%. As non-aqueous solvent
15 additives, there come into consideration especially polar organic solvents, such as e.g. alcohols or acid esters. The reaction can be carried out not only in an open vessel but also in an autoclave, whereby it can be expedient to work in an inert gas atmosphere, e.g.
20 under nitrogen.

If desired, the condensation products can be isolated from their solutions or dispersions obtained after the reaction, e.g. by evaporation on a rotary evaporator or by spray drying. However, the solutions
25 or dispersions obtained can also be used directly as such.

As aldehyde and ketone starting materials, there are used the above-mentioned aldehydes and ketones, whereby mixtures of ketones and/or of aldehydes can
30 also be used. The aldehydes and ketones can be used not only in pure form but also as compounds with the acid group-introducing material (e.g. as bisulphite addition compound). They can be taken or added not only in aqueous but also in non-aqueous, for example
35 alcoholic solution.

-12-

Furthermore, to a partial amount of the ketone, which is mixed with or has already been reacted with the acid group-introducing compound, there can first be added the remaining amount of the ketone, as well as
5 partial amount of aldehyde and finally mixed with the remaining amount of the aldehyde.

This production principle can also be employed in the case of exchanging aldehyde and the ketone. It is especially suitable for the continuous form of the
10 production process.

In the case of aldehydes and ketones with lower alkyl chain, the reaction proceeds especially quickly and exothermally, whereas in the case of compounds with sterically-demanding substituents, such as e.g. methyl
15 isobutyl ketone or benzylacetone, a long thermal after-treatment is necessary for the complete reaction.

As acid group-introducing compounds, there can be used all compounds introducing the acid groups under the condensation conditions, such as e.g. the pure
20 acids, salts of the acids with mono- to trivalent inorganic or organic cations or addition compounds, especially addition compounds with the aldehydes and ketones used according to the invention. Examples therefor are sulphites, hydrogen sulphites, pyro-
25 sulphites, bisulphite addition compounds of aldehydes or ketones, amidosulphonic acid salts, taurine salts, sulphanilic acid salts; hydroxymethanesulphinic acid salts; aminoacetic acid salts; phosphorous acid salts.

The condensation products used according to the
30 invention possess, besides the acid groups, a content of hydroxyl groups, keto groups and possibly double bonds. This clearly follows from their IR spectra which display all the bands characteristic for these groups.

-13-

The following Examples explain the invention in more detail without limiting it thereto. If not stated otherwise, parts and statements of percentages signify parts by weight and percentages by weight.

- 5 The Table I gives a survey of the starting products and the methods of production employed in the production Examples.

- 14 -

T A B L E I

Exa- mple	Starting materials		acid group- introducing substance	mole ratio of ketone: aldehyde: acid group	method of production
	ketone	aldehyde			
A. 1	Acetone	Formaldehyde	sulphite	1:3:0.5	Variant I
A. 2	Acetone	Formaldehyde	sulphite	1:1.67:0.67	Variant I
A. 3	Acetone	Formaldehyde	sulphite	1:1:0.05	Variant I
A. 4	Acetone	Formaldehyde	amidosphonic acid	1:3:0.5	Variant I
A. 5	Acetone	Formaldehyde	aminoacetic acid	1:3:1	Variant I
A. 6	Acetone	Formaldehyde	oxymethanesulphinic acid	1:2:1	Variant III
A. 7	Acetone	Acetaldehyde	sulphite	1:2:0.5	Variant I
A. 8	-	Crotonaldehyde	acetone bisulphite adduct	1:2:1	Variant IV
A. 9	Acetone	Crotonaldehyde/ furfural	sulphite	1:2:0.5	Variant I
A. 10	Acetone	Glyoxal	taurine	1:1.5:0.5	Variant I
A. 11	Methyl ethyl ketone	Formaldehyde	sulphite	1:2:0.75	Variant I
A. 12	Methyl iso- butyl ketone	Formaldehyde	sulphite	1:2:0.35	Variant V
A. 13	Diacetone alcohol	Crotonaldehyde	pyrosulphite	1:6:0.5	Variant I
A. 14	Mesityl oxide	Formaldehyde	sulphite	1:4:1.3	Variant I
A. 15	Acetophenone	Paraform- aldehyde	sulphite	1:3:1	Variant II
A. 16	4-Acetyl- benzene- sulphonic acid	Crotonaldehyde	sulphite	1:2:0.5	Variant I
A. 17	Acetylacetone	Acrolein	sulphite	1:3:2	Variant I
A. 18	Acetone	Formaldehyde	sulphite	1:3:0.5	Variant I
A. 19	Methyl ethyl ketone	Crotonaldehyde	aminoacetic acid	1:3:1	Variant I
A. 20	Diacetone alcohol	Formaldehyde	sulphite	1:3:0.5	Variant I

-15-

A. Preparation of the condensation products.Example A1.

5 Into an open reaction vessel with a stirrer, internal thermometer and reflux condenser, one success-
ively places 1000 wt. parts of water, 630 wt. parts of sodium sulphite, as well as 580 wt. parts of acetone and stirs intensively for a few minutes. A considerable amount of the sulphite thereby dissolves and the temperature of the reaction mixture increases to 31 to 32°C.

10 One heats the batch to 56°C. internal temperature (acetone reflux) and drops into the reaction mixture a total of 3000 wt. parts of 30% formaldehyde solution (formalin). Because of the strong exothermic reaction,
15 one proceeds in the case of the formalin addition in such a manner that one slowly and uniformly adds the first tenth of the formaldehyde solution and awaits the commencement of the reaction, which manifests itself by the commencing yellow coloration and increased acetone reflux.

20 As soon as the first signs of a reaction are visible, one commences with the cooling. The reaction continues with red coloration of the batch and vigorous acetone reflux. After this initial phase has subsided, one allows the remainder of the formalin to run in and
25 maintains the temperature at 60 to 70°C. by cooling. When the dropping in of the aldehyde is finished, one heats to 90 to 95°C. and treats at this temperature for 1 hour.

30 The cooled solution of the condensation product displays a solids content of 34.5% and a viscosity of 25 cP (= mPas) at 20°C.

The product reduces the viscosity of aqueous dispersions and is suitable e.g. for the liquefaction of deep drilling cement slurries.

-16-

Example A2.

The reaction vessel of Example A1 is supplied with 1260 wt. parts of sodium sulphite, as well as 870 wt. parts of acetone and heated to an internal temperature of 56°C. with intensive stirring.

As soon as this internal temperature is reached, one begins with the addition of a total of 250 wt. parts of 30% formaldehyde solution and initiates the exothermic reaction according to the manner described in Example A1. When the reaction is under way, one adds the remainder of the formalin via a supply vessel and allows the temperature of the solution to increase to 80°C. during the last third of the formaldehyde addition. The deep red, initially low viscosity solution thereby assumes a viscosity of 3000 cP (80°C.). After ending of the formaldehyde addition, one further heats to 90°C. for 30 minutes and removes the final condensation product expediently in a hot state.

The solution of the condensation product is non-pourable (viscosity > 1000 P) at room temperature and displays a solids content of 56.0%. An aqueous solution of the condensate reacts strongly alkaline (pH = 13.5).

The product imparts a very good water retention ability to cement mortars and is suitable e.g. for sticking tiles.

Example A3.

2000 wt. parts of water, 63 wt. parts of sodium sulphite and 580 wt. parts of acetone are intensively stirred in the reaction vessel of Example A1 and heated to 56°C. internal temperature.

As soon as the required temperature is reached and the acetone begins to reflux, one adds thereto a total of 1000 wt. parts of 30% formaldehyde solution (formalin), whereby, by the addition of at first 100 wt. parts of formalin, the exothermal reaction is

-17-

initiated and carried out according to the manner described in Example A1. After ending of the formalin addition, one further heats the brick-red, strongly foaming solution to 90 to 95°C. for 1 hour.

- 5 The cooled solution of the condensation product displays a solids content of 24.0% and a viscosity of 10 cP (20°C.).

The product possesses good tenside action and is suitable e.g. for the production of aeroconcrete.

10 Example A4.

- In the apparatus according to Example A1, 970 wt. parts of amidosulphonic acid are first dissolved in 6000 wt. parts of water and neutralised with 370 wt. parts of calcium hydroxide. The solution of the calcium
15 salt of the amidosulphonic acid reacts very strongly acidic and is rendered alkaline by the addition of a further 100 wt. parts of calcium hydroxide.

- To this quantity of the acid group-introducing material one adds 1160 wt. parts of acetone, heats to
20 56°C., adds a total of 6000 wt. parts of 30% formaldehyde solution according to the manner of proceeding described in Example A1. Subsequently, the orange-red solution, which in part still contains excess calcium hydroxide suspended therein, is condensed for 24 hours
25 at 90°C.

The cooled solution of the condensation product has a solids content of 25%, a viscosity of 15 cP (20°C.) and reacts alkaline.

- The product is usable as dispersion agent e.g.
30 for hydraulic binding agents.

Example A5.

- The reaction vessel of Example A1 is supplied, in the given order, with 2000 wt. parts of water, 750 wt. parts of aminoacetic acid, 400 wt. parts of sodium
35 hydroxide, as well as 580 wt. parts of acetone and

-18-

heated up to an internal temperature of 56°C. with intensive stirring.

As soon as the given temperature is reached, one allows a total of 2430 wt. parts of 37% formalin solution, which is stabilised with 0.01% isothphalo-bisguanamine, to run, according to the manner described in Example A1, into the reaction mixture maintained at 60 to 80°C. and heats to 90 to 95°C. for 24 hours.

The brick-red solution of the condensation product displays a greenish fluorescence and has a solids content of 38%. Its viscosity at 20°C. amounts to 25 cP.

The condensate possesses dispersing properties and lowers e.g. the viscosity of deep drilling cement slurries.

Example A6.

In the open reaction vessel of Example A1, 1000 wt. parts of water and 580 wt. parts of acetone are heated to 56°C. with vigorous stirring and adjusted at this temperature to a pH value of at least 13.0 with 38 wt. parts of solid sodium hydroxide.

Subsequently, one allows a clear solution of 1180 wt. parts of sodium formaldehyde sulfoxylate (oxymethanesulphinic acid sodium salt), 1627 wt. parts of 37% formalin (stabilised with 10% methanol) and 3000 wt. parts of water to run into the vessel in the manner of Example A1 and carries out the reaction as described. After the finishing of the formalin addition, one further heats the deep red solution for 5 hours to 90 to 95°C.

The low viscosity solution of the condensation product displays a solids content of 28% and reacts strongly alkaline.

The condensate possesses dispersing and tenside properties.

-19-

Example A7.

5000 wt. parts of water, 1260 wt. parts of sodium sulphite and 1160 wt. parts of acetone are vigorously stirred in the reaction vessel of Example A1 and heated to 56°C. Into this material, one allows, according to Example 1, a total of 1760 wt. parts of pure acet-aldehyde to run in and, after ending of the aldehyde addition, further keeps at 90 to 95°C. for 4 hours.

The orange-brown condensate possesses a solids content of 40% and displays a viscosity of 450 cP at 20°C.

The condensation product displays surface activity and strongly lowers e.g. the surface tension of aqueous solutions.

15 Example A8.

537 wt. parts of acetone-sodium bisulphite adduct are first stirred into 1000 wt. parts of water and the colourless, clear solution adjusted to pH = 13 with 160 wt. parts of solid sodium hydroxide.

20 Subsequently, one supplies the reaction vessel of Example A1 with 1000 wt. parts of water and 464 wt. parts of crotonaldehyde, heats to 60°C. and drops in the above prepared alkaline solution of the acetone-bisulphite adduct according to the manner described in A1. Subsequent to the addition, the batch is further kept at 90 to 95°C. for 3 hours.

The red-brown, low viscosity solution of the condensation product displays a solids content of 30% and reacts strongly alkaline.

30 The product displays surface-active properties and is suitable e.g. for the production of aeroconcrete.

Example A9.

Into the reaction vessel of Example A1 are successively placed 6000 wt. parts of water, 630 wt. parts of sodium sulphite, as well as 580 wt. parts of

-20-

acetone and heated to 56°C. with vigorous stirring.

When the reaction mixture has reached this temperature, one allows a mixture of, in all, 960 wt. parts of furfural and 700 wt. parts of crotonaldehyde to run into the reaction mixture according to the manner described in Example A1. After ending of the addition, it is after-treated at 90 to 95°C. for 4 hours.

The deep red solution of the condensation product displays a solids content of 27% and a viscosity of 180 cP at 20°C.

The condensate is suitable as a dispersion agent with surface-active properties.

Example A10.

One supplies the reaction vessel of Example A1 successively with 2000 wt. parts of water, 625 wt. parts of taurine, 200 wt. parts of solid sodium hydroxide, as well as 580 wt. parts of acetone and heats the reaction material to 56°C. (acetone reflux).

As soon as this internal temperature is reached, one begins with the addition of a total of 2900 wt. parts of 30% glyoxal solution and carries out the reaction, proceeding with strong heat evolution, according to the manner described in Example A1. After ending of the glyoxal addition, one heats to 90 to 95°C. for 2 hours.

The dark red, low viscosity solution displays a solids content of 35% and reacts weakly alkaline.

The condensation product represents a good dispersion agent.

Example A11.

In a pressure vessel of V2A steel with bladed stirrer, internal thermometer and pressure indicator are placed 1500 wt. parts of water, 1890 wt. parts of sodium sulphite, as well as 1440 wt. parts of methyl ethyl ketone and, after the closure of the reaction

-21-

vessel, intensively stirred.

One now heats the material to 70°C. internal temperature and feeds a total of 4000 wt. parts of 30% formaldehyde solution into the pressure vessel via a measuring pump with autoclave inlet, whereby the temperature of the reaction material may increase to at most 85°C. and a maximum overpressure of 2 bar results. After ending of the formalin addition, one further heats the solution to 90 to 100°C. for 1 hour.

10 The orange-red, strongly foaming solution possesses a solids content of 48% and a viscosity of 1200 cP.

 The condensation product is surface-active and is suitable e.g. as air pore former for mortar or concrete.

Example A12.

 In the reaction vessel according to Example A1, one successively places 1000 wt. parts of water, 126 wt. parts of sodium sulphite, 1000 wt. parts of methyl isobutyl ketone, as well as 600 wt. parts of 30% formaldehyde solution and heats the two-phase mixture to 90°C. for 8 hours. The reaction takes place with the visible decrease of the organic phase as a result of condensing in of the methyl isobutyl ketone and yellow coloration of the aqueous phase.

 When the reaction is finished, one separates off the uppermost organic layer, which consists of about 70% of the employed, non-condensed methyl isobutyl ketone, from the aqueous phase. The ketone thus obtained can be re-used for further batches.

 The aqueous, yellow-coloured solution of the condensation product displays a solids content of 14% and reacts strongly alkaline. The viscosity of the solution at 20°C. amounts to 12 cP.

-22-

Because of its surface-active properties, the product is suitable e.g. for air pore introduction into mortar or concrete.

Example A13.

5 In the reaction vessel of Example A1 are successively placed 6000 wt. parts of water, 475 wt. parts of sodium pyrosulphite, as well as 580 wt. parts of diacetone alcohol and heated to an internal temperature of 70°C. As soon as the clear, colourless
10 solution has reached this temperature, one adds thereto 257 wt. parts of solid sodium hydroxide.

To this material one allows a total of 2100 wt. parts of crotonaldehyde to run in in the manner described in Example A1 and, after completion of the
15 aldehyde addition, maintains at 90°C. for 30 minutes.

The deep red solution of the condensation product displays a solids content of 36% and reacts strongly alkaline. Its viscosity at 20°C. amounts to 150 cP.

The product possesses very good tenside
20 properties.

Example A14.

200 Wt. parts of water, 980 wt. parts of mesityl oxide, as well as 1638 wt. parts of sodium sulphite are intensively stirred in the reaction vessel of Example
25 A1 and heated to 90°C.

To the suspension one adds a total of 4000 wt. parts of 30% formaldehyde solution in the manner of Example A1 and further treats the dark red, highly viscous solution at 90 to 95°C. for 1 hour.

30 One obtains a condensation product which is almost solid at room temperature but is water-soluble, which displays a solids content of 50% and reacts strongly alkaline. (pH = 13.5).

-23-

The product increases the viscosity of aqueous solutions and is suitable e.g. as thickening agent for cement slurries.

Example A15.

5 A colourless solution of 900 wt. parts of para-formaldehyde and 1260 wt. parts of sodium sulphite in 3000 wt. parts of water is slowly and uniformly mixed at 60°C., with vigorous stirring, with a total of 1200 wt. parts of acetophenone in the open reaction
10 vessel of Example A1, whereby the temperature of the reaction material must not exceed 70°C. After ending of the ketone addition, one treats the strongly foaming solution at 90 to 95°C. for 2 hours.

15 The yellow coloured, low viscosity solution displays a solids content of 49% and reacts strongly alkaline. The viscosity at 20°C. amounts to 40 cP.

The condensate possesses surface-active properties and is suitable e.g. as a foamer additive for aerated concrete production.

20 Example A16.

 An 80°C. hot solution of 555 wt. parts of 4-acetylbenzene-sulphonic acid sodium salt and 158 wt. parts of sodium sulphite in 2000 wt. parts of water is mixed in the reaction vessel of Example A1 with 23 wt.
25 parts of solid sodium hydroxide.

 Into this strongly alkaline-reacting material one allows to run in, according to the manner described in Example A1, a total of 350 wt. parts of crotonaldehyde in the temperature range of 60 to 70°C. and maintains
30 the batch at 95°C. for 6 hours.

The deep red solution of the condensation product displays a solids content of 33% and reacts strongly alkaline. The viscosity at 20°C. amounts to 12 cP.

The product possesses tenside properties and lowers the surface tension of aqueous solutions.

Example A17.

A vigorously stirred mixture of 1000 wt. parts of acetylacetone, 2520 wt. parts of sodium sulphite and 7000 wt. parts of water is heated to an internal temperature of 60°C. in the reaction vessel of Example A1 and mixed with a total of 1680 wt. parts of acrolein according to the there-described process. Subsequently, one carries out a 4 hour after-heating of the batch at 90 to 95°C.

The deep red condensate possesses a solids content of 40% and displays a viscosity of 24 cP at 20°C.

The product forms considerable foam in aqueous solution and is suitable e.g. as foamer additive for aeroconcrete production.

Example A18.

In a stirrer vessel provided with storage vessel and condenser, 1000 wt. parts of 30% formalin and 580 wt. parts of acetone are intensively stirred with 100 wt. parts of potassium carbonate, whereby the temperature of the batch must not exceed 55°C.

After 12 h., one mixes the acetone-formaldehyde condensate obtained with 1700 wt. parts of water, as well as 630 wt. parts of sodium sulphite, heats to 60°C. and adds thereto a further 2000 wt. parts of 30% formalin, whereby the temperature of the reaction material is increased to 90°C. Subsequently, one carries out a one hour after-heating of the batch at 95°C.

The solution obtained of the condensation product displays a solids content of 30% and is suitable e.g. as liquefying additive for aqueous β -hemihydrate gypsum slurries.

Example A19.

In the reaction vessel of Example A18, 6400 wt. parts of water, 1400 wt. parts of crotonaldehyde, as

-25-

well as 720 wt. parts of methyl ethyl ketone are mixed, with intensive stirring, with 100 wt. parts of potassium carbonate and maintained for 5 h. at a temperature of 80 - 90°C.

- 5 Subsequently, one adds thereto a solution of 970 wt. parts of sodium aminoacetate in 800 wt. parts of water, heats to 80°C. and adds thereto a further 700 wt. parts of crotonaldehyde, whereby the temperature of the batch is to increase slowly to 90°C. At this
10 temperature, one finally carries out a two hour after-heating of the reaction material.

The solution obtained of the condensation product is deep red coloured and displays a solids content of 36%. It possesses surface-active properties.

15 Example A20.

- 1400 wt. parts of water, 1400 wt. parts of 30% formalin solution, as well as 1160 wt. parts of diacetone alcohol are, after the addition of 100 wt. parts of potassium carbonate, intensively stirred in
20 the reaction vessel of Example A18 for 8 hours at 30°C.

- One mixes the yellow coloured diacetone alcohol-formaldehyde condensate with 630 wt. parts of sodium sulphite, heats the batch to 60°C. and adds thereto a further 1600 wt. parts of 30% formalin solution,
25 whereby the temperature of the solution is to reach 90°C. In the course of the one hour after-heating at 90°C., the viscosity of the resin solution increases continuously so that, 30 minutes after the end of the formalin introduction, a further 1500 wt. parts of
30 water must be added thereto in order to maintain the stirrability of the batch.

- The deep red coloured condensation product displays a solids content of 32% and solidifies upon cooling to room temperature. The viscosity of a 10%
35 dilution of this solution amounts to 55 cP.

-26-

The product acts as retention agent and reduces e.g. the water loss of deep drilling cement slurries to porous formations.

B. Examples of use.

5 Example B1.

Liquefaction of deep drilling cement slurries.

10 A condensation product produced according to Examples A1, A5, A10 or A18 lowers the viscosity of deep drilling cement slurries which were produced according to the Standard conditions of API RP 10B and measured with a Fann viscometer.

Example B2.

Dispersion of Portland cement and β -hemihydrate gypsum.

15 The dispersion action of condensation products according to the invention on Portland cement of class 45F, as well as on β -hemihydrate gypsum, is shown in Table II:

T A B L E II

Increase of the extent of spreading of aqueous Portland cement and β -hemihydrate gypsum slurries in the case of the addition of condensation products

condensation product of	Preparation Example	Increase of the extent of spreading of	
		Portland cement slurries ⁺	β -hemihydrate gypsum slurries ⁺⁺
Acetone/formaldehyde/sulphite	A.1	58%	52%
Acetone/formaldehyde/sulphite	A.2	33%	40%
Acetone/formaldehyde/aminooacetic acid	A.5	49%	47%
Acetone/glyoxal/taurine	A.10	54%	49%
Methyl ethyl ketone/formaldehyde/sulphite	A.11	42%	43%
Acetone/formaldehyde/sulphite	A.18	53%	49%

+ amount of condensation product in each case 0.2% of solids, referred to cement content

++ amount of condensation product in all cases 0.8% of solids, referred to gypsum content.

Example B3.Liquefying action of temperature-treated condensation products on deep drilling cement.

5 Table III describes the change of the extent of spreading of an aqueous deep drilling cement slurry in the case of the addition of condensation products treated as follows:

- 10 a) solution of the condensation product according to the preparation Example without additional temperature treatment;
- b) 20% aqueous solution of the condensate autoclaved at the given temperatures for 5 hours;
- c) powder substance of the condensation product after storage for 15 hours at the given temperatures.

TABLE III
Liquefying action of temperature-treated condensation products on deep
drilling cement slurries

condensation product of	Pro- duction Example	change of spreading out of the deep drilling cement slurries +			
		a) condensate solution according to production Example	b) condensate solution 5 h. temperature treated at	c) powdered sub- stance 15 h. temper- ature treated at	
			105°C.	250°C.	250°C.
Acetone/formaldehyde/ sulphite	A1	+ 43%	+ 43%	+ 42%	+ 43%
Acetone/formaldehyde/ aminoacetic acid	A5	+ 30%	+ 30%	+ 30%	+ 30%
Acetone/glyoxal/ taurine	A10	+ 41%	+ 41%	+ 40%	+ 40%

+ production of the slurry according to API RP 10B from class G cement; amount of condensation product in each case 0.2% solids, referred to cement content.

-30-

Example B4.Production of flowing concrete with the addition of dispersing condensation products.

5 Condensation products produced according to
Examples A1, A5, A10 and A18 are suitable for the
production of flowing concrete according to the
instructions of "Directions for the production and
working up of flowing concrete" in the edition of
May, 1974, as are cited e.g. in the periodical "Beton",
10 24, 342 to 344 (1974).

Example B5.Surface activity of condensation products.

15 From pulverised condensation products, each of
which had been stored for 15 hours at 105°C. or 200°C.,
there were stirred up 2% aqueous solutions and their
surface tensions determined tensiometrically. The
measurement results are summarised in Table Iv:

-31-

TABLE IV

Surface tension of 2% aqueous solutions of temperature-treated condensation products

5	condensation product of	production Example	surface tension (dyn/cm)	
			powder at 105°C.	powder at 200°C.
	acetone/acetaldehyde/sulphite	A7	36.2	36.4
10	methylethyl ketone/formaldehyde/sulphite	A11	38.0	38.0
15	methyl isobutyl ketone/formaldehyde/sulphite	A12	33.0	33.0
	diacetone alcohol/crotonaldehyde/pyrosulphite	A13	38.8	39.0
20	acetylacetone/acrolein/sulphite	A17	41.2	41.1

Example B6

Production of aeroconcrete with surface-active condensation products.

25 The 1% solution of the solid condensate of production Example A7 was foamed by means of a commercially-available foam aggregate to a foam of the average density of 0.1 g/cm^3 and stirred into a mixture of 300 kg. of Portland cement 45F, 600 kg. of fine sand (grain size 0 to 1 mm.), as well as 120 kg. of water.

30 The aeroconcrete so produced had a fresh green density of 0.99 g./cm^3 .

Example B7.

Aeroconcrete adhesives with mortar or cement glue in the case of the addition of retention agents.

-32-

Condensation products produced according to Examples A2 and A14 can be used for the production of mortars or cement glues with high water retention ability such as are used e.g. for aeroconcrete adhesions.

The aeroconcrete is so securely adhered by the cement glue that, after 24 hours, no breakage any longer takes place in the joint.

The same result is achieved with solid condensation products which have been temperature-treated for 15 hours at 200°C. and subsequently added to the cement glue as retention agent.

Example B8.

Condensation products produced according to Examples A2, A14 and A20 increase the viscosity of aqueous solutions or of aqueous suspensions of inorganic binding agents, such as e.g. deep drilling and Portland cement or gypsum.



-33-

Claims

1. Use of acid group-containing thermostable, hydrophilic condensation products of
 1. aldehydes and
 - 5 2. symmetrical or asymmetrical ketones with acyclic aliphatic, araliphatic and/or aromatic radicals, whereby, however, at least one radical is a non-aromatic radical,as dispersion agents for inorganic binding agent
- 10 suspensions and solutions, for aqueous kaolin or clay suspensions and for oil-water-coal suspensions, as thickening agents, retention agents and/or liquefying agents, especially for aqueous systems.
2. Use of a condensation product according to
- 15 claim 1 which, as acid groups, contains carboxy, phosphono, sulphino, sulpho, sulphamido, sulphony, sulphoalkyloxy, sulphinoalkyloxy and/or phosphonooxy groups for the purpose of claim 1.
3. Use of a condensation product according to
- 20 claim 1 or 2, in which the mole ratio of ketone/aldehydes/acid group-introducing compounds is 1/1 to 6/0.02 to 2 for the purpose of claim 1.